Indian J. Phys. **75A** (4), 467-469 (2001)

IJP
— an international journal

Anisotropic Heisenberg exchange in a 3-D copper compound

Sarmila Datta and A K Pal*

Department of Solid State Physics, Indian Association for the Cultivation of Science, Kolkata-700 032, India

E-mail : sspakp@mahendra.iacs.res.in

Abstract : X-band EPR investigations on copper malonate dihydrate are carried out in the temperature range 300K-77K. Although two types of Cu(II) ions having square bipyramidal and square pyramidal coordinations are present in the crystal only a single-line spectrum having Lorentzian lineshape is observed in all directions of the crystal in the magnetic field range, 0-8000Oe employed in the experiment. The linewidth varies in the range 85-1170e, having maximum value along crystallographic c-axis. To evaluate the various interactions responsible for anisotropic linewidth in the principal crystallographic planes, the fitting of linewidth is done, following well known linewidth expression of Anderson and Weiss applicable for 3D magnetic solids. Additional contribution from hyperfine interaction is also considered but the fitting is not at all satisfactory. However, it has been shown that introduction of anisotropic Heisenberg exchange (J) in the linewidth expression of the form $J = J_a \cos^2\alpha + J_c \sin^2\alpha$ (where J_a and J_c are the exchange parameters along *a*- and *c*-directions respectively and α is the angle between the applied magnetic field and a-direction) has provided excellent fitting of linewidth in (010) plane. Similar agreement in fitting linewidth anisotropy in (100) plane has been obtained using a similar expression of the anisotropic Heisenberg exchange. From above fitting, it is also evident that the anisotropy in exchange is anomalously large compared to the value of average exchange. It is proposed that the unusually large anisotropy in exchange has its origin in the exchange between relatively closely placed equivalent and inequivalent copper ions along the c-axis which is large compared to that along the other two principal crystal axes (a, b).

Keywords . EPR, copper malonate dihydrate, 3D-magnetism

PACS No. 76.30.-v

1. Introduction

Existence of several copper malonate compounds has been reported by several groups [1-4]. Copper malonate dihydrate (in brief, CMDH) belong to orthorhombic class having space group *Pbcn* [5]. Two types of Cu(II) ions having different ligand coordinations are present. The structural parameters and the bond lengths around the two types of Cu-atoms are given in Table 1. Atom Cu(1) (Figure 1) adopts square bipyramidal coordination. The base of the coordination polyhedron is formed by four oxygen atoms from two malonate ions, while the two apieces are formed by two oxygen atoms from water molecules. The four basal copper-oxygen bonds are of equal magnitude, while the axial bonds are longer. The coordination about Cu(2) is square pyramidal. Here, the base of the pyramid is formed by three oxygen atoms from malonate ions and one oxygen atom from water molecules. The apex of the pyramid is formed by one oxygen atom from a malonate ion. The bond lengths forming the base of the pyramid are nearly equal, while the axial bond is longer. From structure, it is also seen that the two kinds of Cu^{2+} ions are weakly coupled through O(11) and O(110) ligand atoms. Cu(1)-Cu(2) distance being 5.78Å. Magnetic susceptibilities and electron paramagnetic resonance (EPR) studies of the powdered sample deliver contradictory results. Magnetic susceptibility shows peculiar magnetic moment variation in the 80-297K temperature range, the substance having anomalous magnetic moment at 80K, *i.e.* μ per Cu^{2+} ion = 2.71 Bohr magneton [5]. Powder EPR depicts a broad spectrum at room temperature (RT)

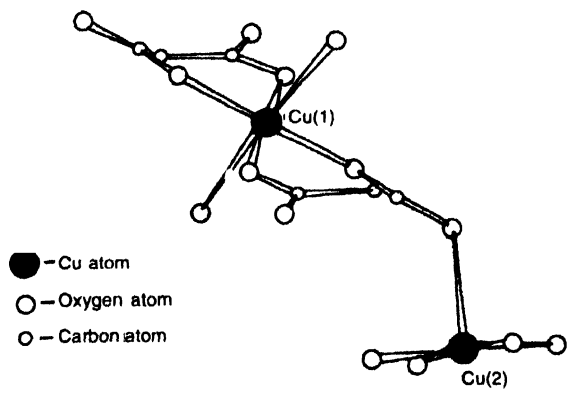

Figure 1. Coordination sphere of Cu(1) and Cu(2) sites in copper malonate dihydrate.

* Corresponding Author

which transforms into two anisotropic spectra at liquid nitrogen temperature (LNT).

With a view to resolve the above anomalous situation *i.e.* whether Cu(1) and Cu(2) units of 'copper dimers' are coupled or independent from the point of view of magnetic exchange, single crystal EPR investigations are carried out at X-band in different crystallographic planes of the crystal in the temperature range, RT-77K.

2. Experimental

To a suspension of basic copper (II) carbonate in water-bath, malonic acid is added in small portions with stirring, allowing effervescence to subside between subsequent additions. This process is continued until 20% of basic copper carbonate remained unreacted. The hot reaction mixture is filtered, and the filtrate is allowed to evaporate at room temperature, when blue crystals of the compound appear. They are filtered off, washed twice with cold water and then dried over fused calcium chloride [5].

EPR derivative absorption spectra are recorded with a Varian X-band E-line (E-109) century series EPR spectrometer at RT and LNT in (010), (001) and (100) planes of CMDH crystal.

3. Results and discussion

Only a single-line spectrum having Lorentzian line shape is observed in all directions in the magnetic field range 0-8000Oe employed in the experiment. This signifies that the exchange interaction existing between nearest magnetically inequivalent Cu(110) ions in the crystal is of sufficient magnitude to average out the individual spectra due to these ions at X-band.

No detectable change either in g-factor or linewidth or lineshape has been noticed in the temperature range RT-LNT.

A. g-vlaues :

From measurements in (010) and (100) planes, the principal crystalline g-factors, g_a, g_b, and g_c are obtained, where g_a, g_b, g_c are principal crystalline g-factors along a, b and c axes respectively. EPR signals due to magnetically inequivalent Cu^{2+} complexes in the unit cell can not be resolved, and so the simplifying assumption of tetragonal symmetry of the ligand field around each copper (II) ion is made to derive the principal ionic g-factors ($g_\parallel$ and $g_\perp$) from crystalline g-factors with the help of the following relations :

$$g_\parallel^2 - g_\perp^2 = g_a^2 - g_b^2 / (\alpha^2 - \beta^2) = g_b^2 - g_c^2 / (\beta^2 - \gamma^2)$$

$$= g_c^2 - g_a^2 / (\gamma^2 - \alpha^2), \qquad (1)$$

$$g_\parallel^2 + 2g_\perp^2 = g_a^2 + g_b^2 + g_c^2, \qquad (2)$$

where α, β and γ are taken to be the mean direction cosines of $g_\parallel$ direction with respect to a, b, c axes of the crystal calculated from the X-ray structural study [5] given by the following relations :

$$\alpha = \alpha_1 + \alpha_2 / 2;\ \beta = \beta_1 + \beta_2 / 2;\ \gamma = \gamma_1 + \gamma_2 / 2.$$

$\alpha_1, \beta_1, \gamma_1$ and $\alpha_2, \beta_2, \gamma_2$ are the direction cosines of $g_\parallel$ directions with a, b and c-axes of the crystal of Cu(1) and Cu(2) sites respectively.

Table 1. Structural parameters of copper malonate dihydrate

Space Group : *pbcn*

a = 14 86 Å, b = 14 99 Å, c = 12 65 Å, Z = 8

Co-ordination around Cu(1) (Square bipyramidal)			
Cu(1)–O(11)	1 95 Å	Cu(1) O(14)	1 94 Å
Cu(1)–O(12)	1 95 Å	Cu(1)–O(15)	2 41 Å
Cu(1)–O(13)	1 95 Å	Cu(1)–O(16)	2 51 Å
Co-ordination around Cu(2) (Square pyramidal)			
Cu(2)–O(21)	1 93 Å	Cu(2)–O(24)	1 92 Å
Cu(2)–O(22)	1.92 Å	Cu(2)–O(110)	1 39 Å
Cu(2)–O(23)	1 93 Å		

Values of $g_\parallel$, $g_\perp$ so derived, along with those of g_a, g_b and g_c are shown in Table 2.

Table 2. g values

Compound	g_a	g_b	g_c	$g_\parallel$	$g_\perp$
Copper malonate dihydrate	2 11	2 11	2 27	2 31	2 08

B. Linewidth :

The observed angular variation of linewidth in (010) and (100) planes are shown in Figure 2. The linewidth varies in the range 85O*e* – 117O*e*, having maximum value along crystallographic c axis.

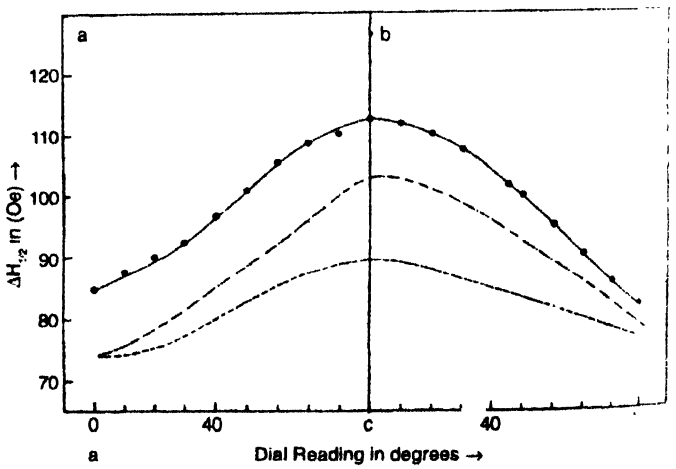

Figure 2. $\Delta H_{1/2}$ *vs* orientation in the (a) (010) and (b) (100) planes of Copper malonate dihydrate ; (●●) Experimental points; Theoretical curves considering : (---) dipolar and isotropic exchange interactions (-·-) dipolar hyperfine and isotropic exchange interactions, (—) dipolar, hyperfine, and anisotropic exchange interactions.

Lineshape is Lorentzian, as derived by applying normalization technique to the observed derivative spectra [6]. This is true for all spectra obtained in different directions. So it is straightforward to derive half amplitude linewidth $\Delta H_{1/2}$ from observed derivative linewidth ΔH_{pp} using the relation $\Delta H_{1/2} / \Delta H_{pp} = \sqrt{3}$. To evaluate the various interactions responsible for observed anisotropic linewidth in different crystallographic planes the fitting of the linewdith has been done following the linewdith expression of Anderson and Weiss [7] applicable in case of three dimensional (3D) magnetic solids :

$$\Delta H_{1/2} = 2H_{dip}^2 / H \tag{3}$$

H_{dip} is the usual Van Vleck dipolar second moment. H_{ex} is the exchange field which is given by

$$H_{ex} = [2.83S(S+1)]^{1/2} J / g\beta, \tag{4}$$

where J is the Heisenberg exchange parameter and g is given by

$$g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta. \tag{5}$$

J is taken as a fitting parameter. From Figure 2 it is evident that the fitting of the expression (3) with the observed angular dependence of linewidth is very poor. In order to see whether any improvement in fitting is achieved, additional contribution from hyperfine interactions (H_{hf}) towards the linewidth is also considered.

$$\Delta H_{1/2} = 2(H_{dip}^2 + H_{hf}^2) / H_{ex}, \tag{6}$$

where H_{hf} is given by [8]

$$H_{hf}^2 = 5(A_{\parallel}^2 g_{\parallel}^2 \cos^2\theta + A_{\perp}^2 g_{\perp}^2 \sin^2\theta) / 4g^2(\theta). \tag{7}$$

In absence of a suitable diamagnetic isomorph of CMDH, hyperfine parameters ($A_{\parallel}$, $A_{\perp}$) cannot be evaluated. So, H_{hf} has been estimated using the values of $A_{\parallel}$, $A_{\perp}$ values obtained in the case of octahedral oxygen coordinated Cu^{2+} : zinc malonate [9] From Figure 2, it is seen that there is some improvement in the fitting after inclusion of H_{hf}. But significant disparity still exists between experimental and theoretical curves. Heisenberg exchange parameter J is then considered to be anisotropic. In (010) plane, J is assumed to have the form

$$J = J_a \cos^2\alpha + J_c \sin^2\alpha, \tag{8}$$

where J_a and J_c are the exchange parameters in the a and c directions respectively and α is the angle between the applied magnetic field and a-direction. The observed linewidth data is then fitted to eq. (6) in conjunction with eq. (8), where the criterion for the best fit is to minimize the function

$$F = \Sigma\left(\chi_i^{obs} - \chi_i^{cal}\right)^2 / \Sigma \chi_i^{obs}, \tag{9}$$

where χ_i^{obs} and χ_i^{cal} are the experimental and calculated linewidths respectively. The best fitted parameters are shown in Table 3. It is seen that the fitting is quite excellent. Similar agreement in fitting linewidth anisotropy in (100) plane has been obtained with anisotropic Heisenberg exchange. It is noted that the value of exchange parameter along c-axis is about 10 times greater than that along a or b-axis. From the above linewidth analysis, an interesting observation emerges, that is, while exchange is small, anisotropy in exchange is unusually large. Similar behaviour was observed in $(NH_4)_2CuCl_4.2H_2O$ and $(NH_4)_2CuBr_4.2H_2O$ [10, 11].

Table 3. Estimated values of the exchange parameters and hyperfine parameters

Compound	Exchange parameters cm^{-1}			Hyperfine parameters $\times 10^4$ cm^{-1}	
	J_a	J_b	J_c	$A_{\parallel}$	$A_{\perp}$
Copper malonate dihydrate	0.01	0.01	0.11	99	39

The unusually large anisotropy in Heisenberg exchange may be accounted for by the fact that the exchange interaction among equivalent and inequivalent copper ions along the c-axis which are relatively closely placed compared to those Cu^{2+} ions along other axes, is expected to be very large compared to that along the other two crystal axes. It is also most likely that such arrangement of Cu^{2+} ions may lead to phonon induced exchange interaction [12] dominating along the c-axis.

References

[1] O Asai, M Kishita and M Kubo *J Phys Chem*. **63** 96 (1959)

[2] L Dubicki, C M Harris, E Kokot and R L Martin *Inorg Chem* **5** 93 (1966)

[3] B N Figgis and D J Martin *Inorg Chem* **5** 100 (1966)

[4] H T S Britton and E D Jarrett *J. Chem. Soc.* **168** (1935)

[5] Debashis Chattopadhyay, Shyamal K Chattopadhyay, Phillip R Lowe, Carl H Schwalbe, Sunil K Mazumder, Arindam Rana and Saktiprosad Ghosh *J Chem. Soc. Dalton Trans.* 913 (1993)

[6] *Electron Paramagnetic Resonance : Techniques and Applications*, R S Alger (Interscience) p42 (1968)

[7] P W Anderson and P R Weiss *Rev Mod Phys* **25** 269 (1953)

[8] Z G Soos, T Z Huang, J S Valentine and R E Hughes *Phys Rev* **B8** 993 (1973)

[9] Sarmila Datta *Ph D Thesis* (Jadavpur University, Calcutta, India) (1998)

[10] S Pal, R Samanta and A K Pal *Phys Stat Sol* (b) **179** K37 (1993)

[11] S Pal *Ph D Thesis* (Jadavpur University, Calcutta, India (1994)

[12] R Orbach and M Tachiki *Phys. Rev.* **158** 524 (1967)